

Development of a Test for Evaluation of the Hydrothermal Stability of Sorbents used in Closed-Loop CO₂ Removal Systems

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The International Space Station Carbon Dioxide Removal Assembly uses zeolite 5A molecular sieve material packed into beds for the capture of cabin CO₂. The beds are cyclically heated to drive off the CO₂ and restore the removal capacity. Over time, the sorbent material has been found to break down resulting in dust that restricts flow through the beds. Humidity adsorbed in the 5A zeolite when it is heated is a suspected cause of this sorbent degradation. To evaluate the impact of adsorbed water during thermal cycling, the Hydrothermal Stability Test was developed. The test configuration provides comparative side-by-side flow restriction data for two sorbent materials at specifically controlled humidity levels. While the initial focus of the testing is on 5A zeolite materials currently used on the ISS, the system will also be used to evaluate future candidate materials. This paper describes the approach, the test system, current results, and future testing.

Nomenclature

4BMS	=	4-Bed Molecular Sieve
CDRA	=	Carbon Dioxide Removal Assembly
HST	=	Hydrothermal Stability Test
ISS		International Space Station
LEO	=	Low Earth Orbit
mmHg	=	millimeter of mercury (Torr)
pp	=	partial pressure
slpm	=	standard liters per minute (STP= 0 °C, 760 mmHg)

I. Introduction

Removal of carbon dioxide from the cabin atmosphere is a critical function of any spacecraft's life support system. Minimizing mass, power, and volume is always a prime consideration and, for missions of other than short durations, a regenerative system that requires the least amount of consumables is required. As critical as these factors are, long-term reliability is also of utmost importance. The ISS Carbon Dioxide Removal Assembly (CDRA) is a state-of-the-art system for cabin CO₂ removal that utilizes fixed beds of sorbent pellets and is currently the baseline technology for use in future crewed exploration missions beyond LEO.

The ISS CDRA utilizes a fully regenerative thermal/pressure swing adsorption process that is generically referred to as a 4-Bed Molecular Sieve (4BMS). It operates cyclically and employs two desiccant beds and two adsorbent beds. As one desiccant bed and one adsorbent bed operate in adsorption mode (flow of humid and CO₂

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laden cabin air), the other two beds are desorbing (regenerated with heat and vacuum). Half way through a cycle, the beds switch modes, providing continuous CO₂ removal capability. The thermal swing process allows the system to function in a closed-loop architecture. The closed-loop designation refers to the fact that the CO₂ can be recovered from the 4BMS process and delivered to subsystems that can then recover the O₂ from the CO₂.

The 2 on-orbit CDRA's have operated extensively over a period of several years but an increasing and ultimately excessive differential pressure across the sorbent beds during operation has been a recurring problem. The increase in pressure drop has been traced to the breakdown of the sorbent materials and subsequent blockage of the system filters and screens.¹ Modification of CDRA components and replacement of the original 5A ASRT zeolite cylindrical pellet material with the spherical RK-38 material did not cure the problem. To address this issue, and to identify potential improved materials and processes, an effort to better characterize the current and potential replacement sorbent materials was undertaken.^{2,3}

Tests performed to determine crush strength of the sorbent materials showed a clear sensitivity of the crush strength to absorbed water⁴. This observation, along with the evidence that the on-orbit CDRA with RK-38 sorbent is experiencing higher than expected humidity exposure and that the pressure drop is increasing more rapidly than expected, led to the development of a new test regime.⁵ The Hydrothermal Stability Test (HST) was subsequently developed to evaluate the sorbent material with elevated and controlled humidity levels while being thermally cycled with the same temperature profile as present in the ISS CDRA.

II. Approach for Evaluating Hydrothermal Stability of Sorbents

The primary objective of the HST is to provide simultaneous comparison testing of two 5A molecular sieve sorbents while being conditioned to 4 specific humidity levels and subjected to the thermal cycles and airflow rates as found in the ISS CDRA. The pellet degradation is expected to be progressive and the test is designed to operate for an extended period. There are two parameters of sorbent evaluation criteria for the HST. The first, and most applicable to the on-orbit observations, is the generation of dust as measured by pressure drop increases measured across the downstream screen and filter for each test bed assembly. The second evaluation parameter is the measured crush strength of pellets, which are periodically removed from the test bed assemblies over the duration of the test process. This second criteria required that each test bed volume be sufficient to allow 50 pellets to be removed at least 20 times before the end to the test sequence.

Table 1 lists the flow and humidity of the inlet process gas specified for the adsorption half cycle for each test condition. Reference 5 details the analysis used to derive the inlet humidity conditions but in general, the driest condition represents that which is present in a fully functioning CDRA, while the wettest condition would result in a CDRA with 20% loss of CO₂ removal performance. The 1.38 slpm adsorption flow rate was selected so that the superficial velocity of the process air through the sorbent bed will equal that present in the CDRA sorbent bed.

Table 1. HST Process Gas Humidity and Flow Requirements

Case	Inlet H ₂ O pp, mmHg	Flow Rate, slpm	Dew Point	
			°F	°C
1	< 7.25x10 ⁻⁵	1.38	-130 max	-90 max
2	0.012	1.38	-71	-57
3	0.70	1.38	-6	-21
4	1.38	1.38	7	-14

The temperatures, and perhaps more importantly the rate of temperature change, may be critical components of the observed degradation of the 5A zeolite material. At the same time, the flow restriction observed on the ISS CDRA, took a significant amount of time before becoming an issue. For the HST, a compromise thermal profile was selected that maintains the adsorb and desorb temperatures as well as the rate of temperature change while also compressing the total length of a cycle. Table 2 shows

Table 2. HST Sorbent Temperature Profile

Step	Time, Minutes		Temperature	Ramp Rate
			°C	°C/min
1	0		10	
2	68.5		204.4	2.84
3	72.5		204.4	
4	113.7		10	-4.72
5	145		10	

the time/temperature set points for the HST. The plot in Figure 1 shows the HST thermal profile as compared with the nominal ISS CDRA profile. This thermal profile maintains the critical CDRA thermal parameters while nearly doubling the number of cycles performed in the time available.

Desorption for the ISS CDRA is a thermal/vacuum process with the bed placed under vacuum as it is heated. The vacuum facilitates removal of the water vapor and CO₂ from the bed as the increased heat drives it from the sorbent material. To simplify the design of the HST, the vacuum is replaced by a low flow rate of dry purge gas during the desorption half-cycle. Although the flow rate of the purge gas is not critical, it must be low enough to minimize the cooling effect on the sorbent material, which could cause a thermal gradient across the bed assembly.

As stated earlier, the volume of each test bed is driven by the requirement to allow removal of material for crush testing periodically during the test process. To match the thermal characteristics of a heater channel within the CDRA, a cylindrical tube with an I.D. of 11.1 mm was chosen, resulting in a length of ≈ 165 mm. The cylinder is fabricated from Invar to minimize the possibility of pellet crushing due to the thermal contraction and expansion of the tubing. A drawing of the bed assembly is shown in Figure 2. The inner tube contains the 5A material while the outer tube surrounds the heater and passages for the cooling airflow.

The pellet containment features of the test bed cylinder include a movable screen on the upstream side that can be adjusted as material is removed for testing, and a downstream screen. The downstream screen has 50 μ m openings, which are the same as in the bed screens in the CDRA. Initially the outlet screen was fabricated from a solid end piece, which was then perforated with multiple 50 μ m openings. However, after early test runs yielded inconsistent results, the outlet containment system was redesigned to accommodate a wire mesh screen of a 50 μ m pore size. This configuration more closely matches the CDRA bed containment system.

III. Test Stand Description

A simplified flow schematic for the test stand developed to implement the HST is shown in Figure 3. The test stand is configured with 8 identical test beds that are assembled with instrumentation and control components into 8 test article assemblies. These assemblies, identified as A1 through A8 on the schematic, are paired to allow side-by-side test of the 2 types of zeolite. For the initial testing, the 2 types of 5A zeolite under evaluation are the RK-38, currently in the on-orbit CDRA, and the ASRT which was in the CDRA previously. The test stand incorporates over 100 instrumentation and control channels that are monitored and recorded during all operations.

Details of the test stand temperature control are not shown on the schematic but the entire stand is enclosed in a temperature-controlled chamber that is maintained at 10 °C. This ensures that the process gas is at the same nominal temperature of the air entering the ISS CDRA sorbent bed during the adsorption half-cycle. Each test article assembly incorporates individual heater and cooling airflow control mechanisms. The pairs of test article assemblies are set to alternate half-cycles so that half of the assemblies are in the adsorb half-cycle while the other half are

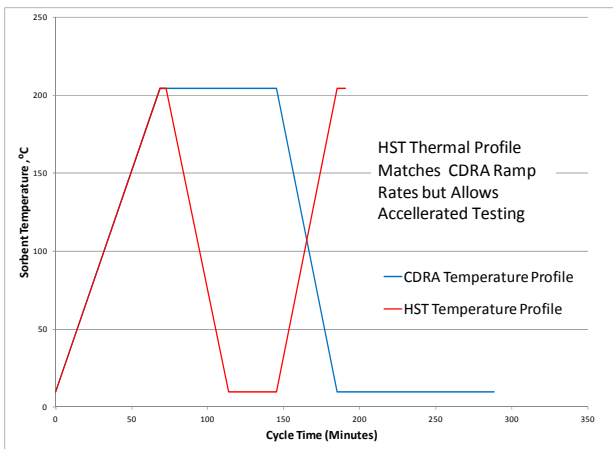


Figure 1. HST vs CDRA Cyclic Temperature Profile

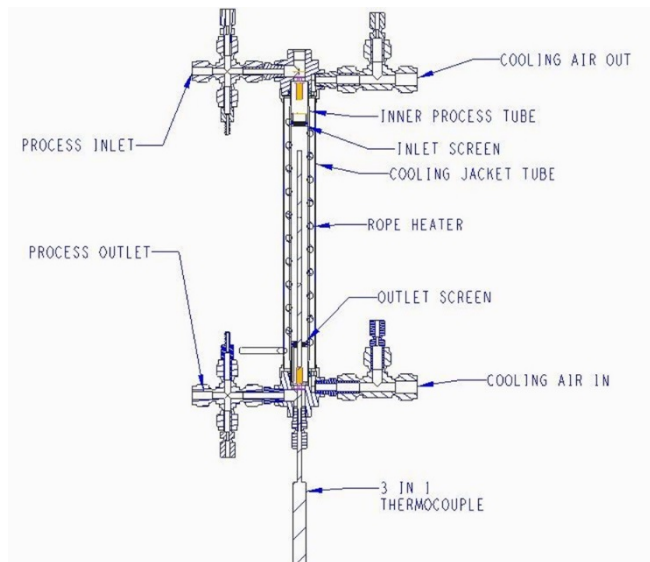


Figure 2. HST Test Bed Configuration

desorbing. Although this configuration requires that the adsorb and the desorb half-cycles be of the same length, it does allow a somewhat simpler sorbent cooling system.

The humidity of the adsorption gas streams are set by controlled mixing of a humidified gas stream with a dry stream. In each case, a constant dry gas flow is maintained while the humidified mix gas flow is controlled to obtain the desired water vapor partial pressure as measured by an in-line hygrometer. The humidified flow rates shown on Figure 3 are nominal values for the adsorb half-cycle. During the desorption half-cycle, the humid gas flow is shut off so that only dry gas is used for the purge flow. The inlet flow conditioning system uses a bypass flow approach that continuously vents excess gas and maintains a constant pressure and flow for gas mixing and measurement. This assures accurate and consistent inlet gas conditions. Each test article assembly has a dedicated flow controller to assure the correct flow through the beds despite the fact that the pressure drop across the assemblies may be different. Assemblies A7 and A8 are provided with dry gas only, although an in-line hygrometer monitors the gas to assure that the humidity does not exceed the requirements. The initial configuration of the test stand used high-purity air for the process gas; however, early testing was impacted by excess humidity, so the stand was converted to use dry nitrogen.

An outlet sample system allows the exiting gas from any of the test beds to be selected and passed through a hygrometer to monitor the humidity of the outflow. The outlet hygrometer can measure the humidity of both the adsorb flow and the purge flow. Although measurement of the outlet humidity is not a primary requirement for the HST, the capability does allow changes in water removal characteristics to be identified and monitored.

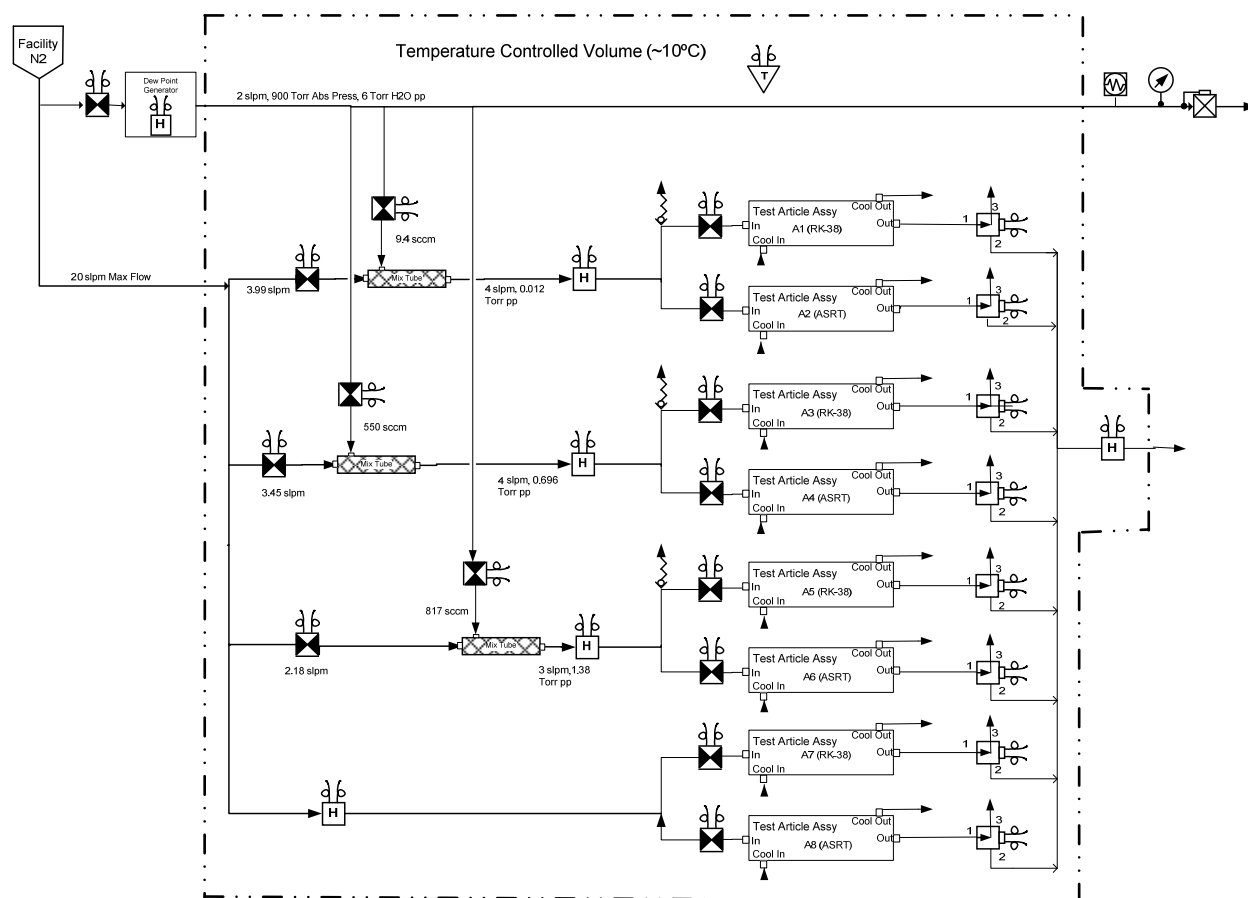


Figure 3. Simplified Flow Schematic of HST Stand

Figure 4 shows the schematic view of a test article assembly. The differential pressure sensor, PD1, measures the pressure drop across the sorbent material and the 50 μm outlet screen, while sensor PD2 measures the drop across a 2 μm sintered stainless steel filter that is placed downstream of the screen to catch smaller dust particles. These differential pressure measurements provide the primary evaluation criteria obtained during HST cyclic operations.

Figure 5 shows a photo of the test stand as assembly was nearing completion. In this view, the test article assemblies (the vertical tubes in the center of the photo) are being insulated. The insulated hoses in the forefront are the cooling air inlet and outlet lines.

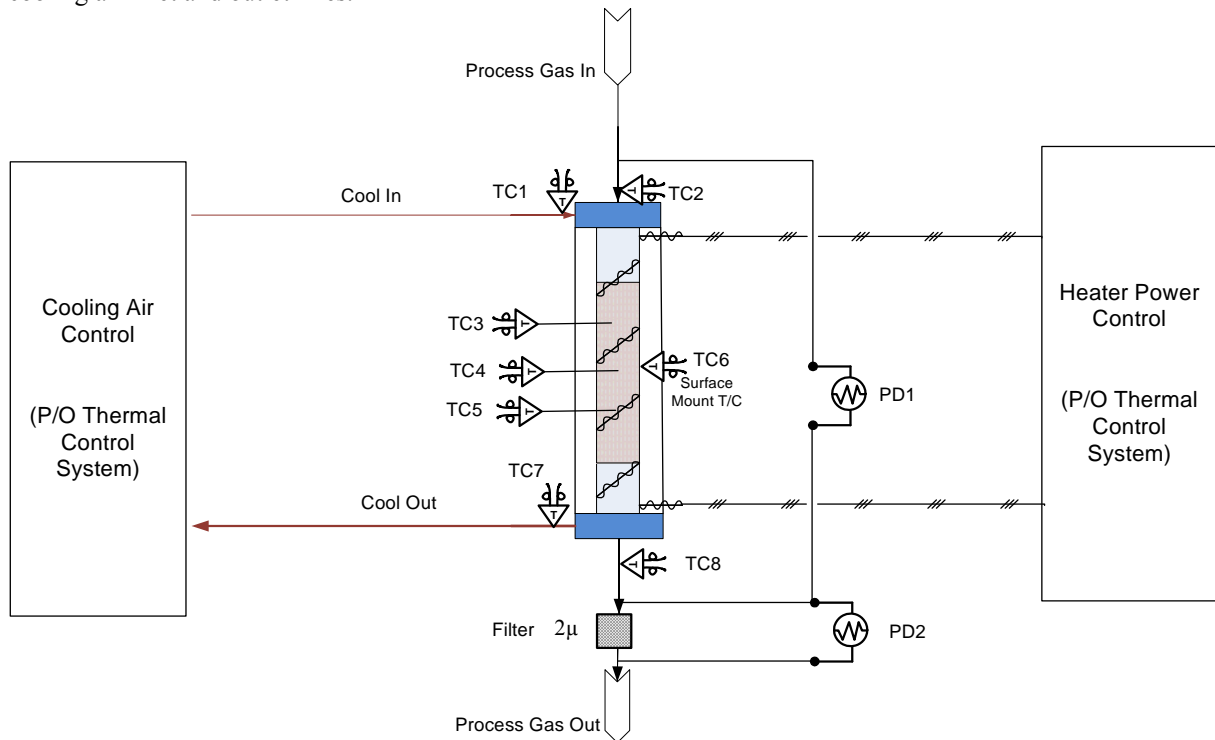


Figure 4. Schematic of Test Article Assembly



Figure 5. HST Test Stand in the Final Stage of Assembly

IV. Test Operations

The HST began operations in July of 2014. The cycle time chosen for HST operations allowed each day to equal almost 2 days of CDRA thermal cycles. Since it was not known how soon any degradation in material strength might be detectable, the initial runs were set to operate for less than the equivalent of one month of CDRA operation.

Figure 6 shows the recorded temperature and inlet humidity conditions for the A4 and A5 test cells over a typical half day of operation. The temperature shown is the average of the 3 internal and the single wall mounted thermocouples. The A4 and A5 assemblies are on alternate half-cycle schedules, which explains why the plot shows that the A4 temperature is rising while the A5 temperature is falling. The A4 cell is a part of the A3/A4 pairing that receives the inlet flow with 0.7 mmHg H₂O pp while the A5 cell, along with the A6 cell, receives the 1.38 mmHg H₂O pp. For both pairs, the water vapor partial pressure of the dry purge during the desorption half-cycle is less than 1×10^{-5} mmHg H₂O. The higher value on the plot for the A5 H₂O pp during the purge is due to range limitations of the hygrometer.

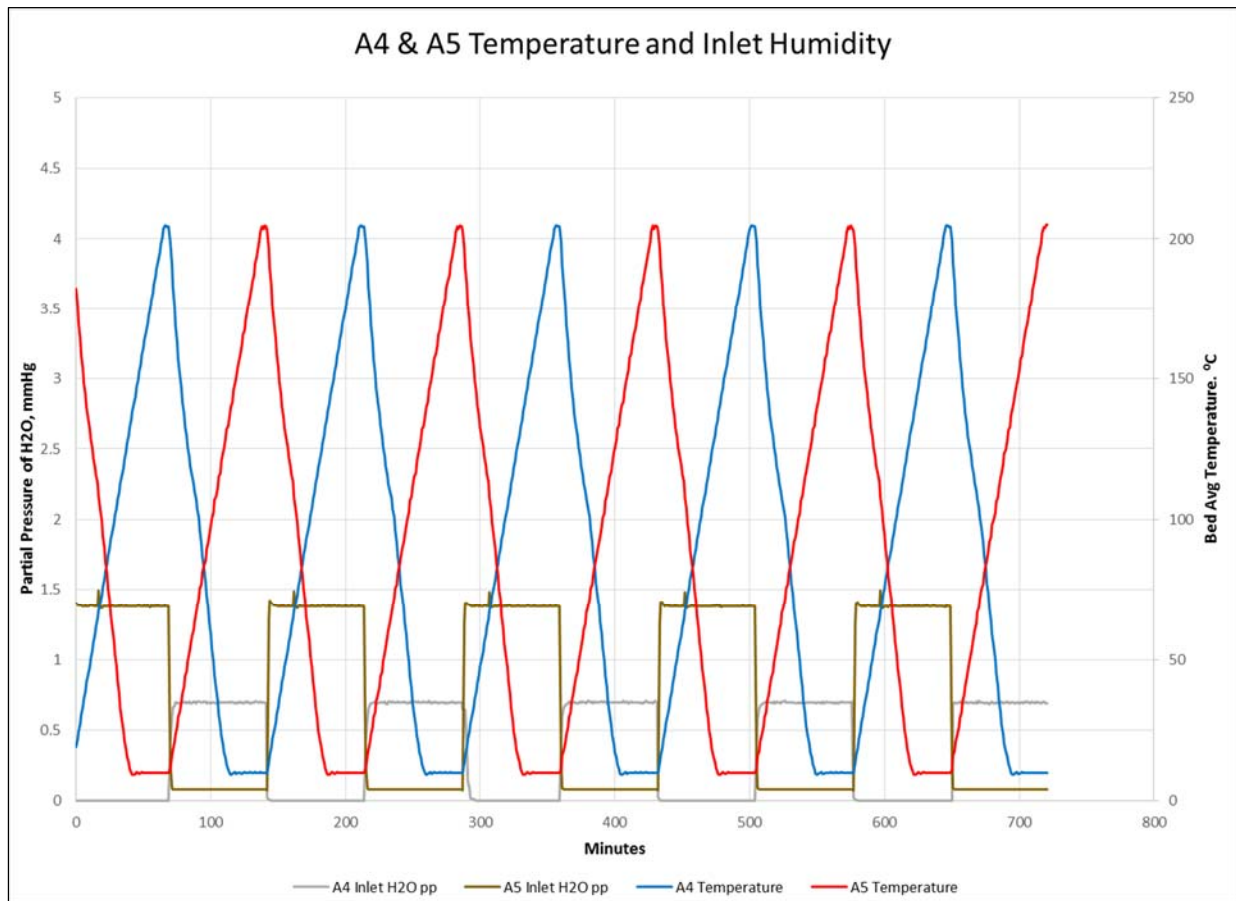


Figure 6. Typical Temperature and Inlet Conditions for 1/2 Day of HST Operations

Figure 7 shows the temperature and inlet/outlet humidity over one cycle for the A4 assembly. As stated previously, the A4 and A5 assemblies receive 0.7 mmHg H₂O pp inlet flow and are in the midrange of the selected humidity test conditions. Due to this, the inlet/outlet humidity levels of the other test cell pairs have different magnitudes, but the general characteristics are similar. The temperature profile for all the assemblies are controlled and are the same for all test assemblies.

Each cycle begins with a desorption half-cycle where the sorbent is heated at the specified rate. A purge flow of 0.1 slpm of dry gas is maintained for the entire half-cycle to displace the water vapor that is driven off the sorbent material. As can be seen in the plot, the water begins to desorb at ≈ 100 °C. The discontinuity seen on the outlet humidity plot as it is rising is actually an artifact of the chilled mirror hygrometer where the frost layer on the mirror transitions to liquid condensation. This characteristic is exacerbated by the low flow rate of the purge.

At the start of the adsorb half-cycle the humidity of the inlet stream is set to the nominal value but the flow rate is set to the minimal value of 0.02 slpm. This low flow prevents the sorbent from cooling too quickly but it also is not sufficient for the outlet hygrometer to track the humidity level. Once the bed has cooled to $\approx 120^\circ\text{C}$, the full 1.38 slpm adsorption flow is set and maintained for the remainder of the adsorb half-cycle.

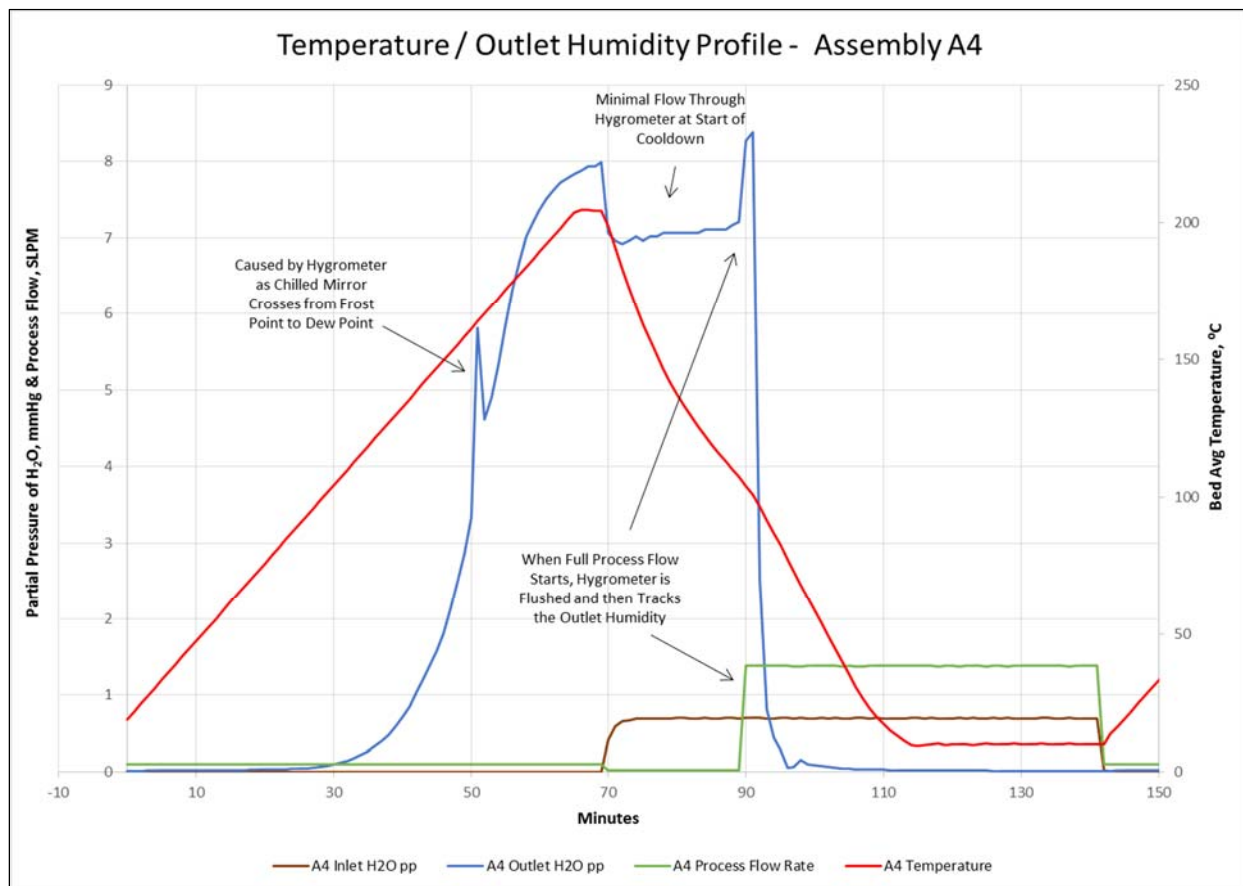


Figure 7. Typical Hydrothermal Profile of an HST Cycle

In addition to cyclic operation, the HST requirements also include removal of some sorbent material for offline strength testing. To accommodate this action, the cyclic testing was periodically suspended and the test article assemblies were removed and disassembled. After removal of the designated number of 5A sorbent pellets, the assemblies were replaced in the test stand and cyclic testing resumed. Each period of uninterrupted cyclic operation is designated as a run and the first 4 runs of cyclic operation were from 12 to 15 days in duration. Table 1 lists the actual duration of each of the completed runs. The longer run is the last one for which data was available for this paper. The ongoing and future test runs are scheduled for similar length durations as Run #5.

Table 3. HST Runs Completed

Run #	Duration, Hours
1	260
2	300
3	380
4	320
5	1056

V. Pressure Drop Results

The primary evaluation criteria produced by cyclic test operations are the pressure drop measurements across the bed assemblies and the post bed filters. The pressure drop across these elements is a function of volumetric flow rate as well as the restriction to flow. Although the adsorb flow is set to a constant mass flow rate, changes in gas temperature have a significant effect on the measured pressure drops. To compensate for this, the HST control software is configured to calculate the average of each pressure drop measurement while the bed temperature is

within 2 °C of the adsorb temperature set point. This calculation is updated for each adsorb half-cycle and is recorded by the data acquisition system.

At the end of each run of cyclic operation, the pressure drop measurement data was analyzed to determine if a statistically significant change in pressure drop could be found and if the results were consistent with prior runs. By the end of the 4th run, however, it became clear that the data was inconsistent between runs and that the testing was not generating statistically significant results. This inconsistency was particularly evident in the initial bed pressure drop measured at the start of each run.

A review of the HST hardware and processes was undertaken to find the cause of the inconsistent results. The review found two major contributors. The primary issue was found to be in the configuration of the outlet screens. The test bed outlet screen was fabricated from a solid end piece, which was then perforated with multiple 50 µm openings. Under microscopic examination, it was found that many of the openings were blocked to varying degrees in the fabrication process. Also in some cases, the openings were blocked by sorbent dust particles that had become lodged in the openings. The process for handling the test beds when removing sorbent material for strength testing was found to be a contributing issue. The method used did not adequately control the amount of dust that remained in the test beds and outlet screens between runs.

To address these issues, the sorbent retaining system was redesigned to use a wire mesh screen with a 50 µm pore size. The wire mesh is more open than the previous design and the geometry of the screen makes it more likely that a dust particle that is too large to pass through, will sit on top of the screen and less likely it will be trapped within the pore. This makes it easier to remove the dust prior to the start of the next run. The process for removing the sample of pellets at the end of a run was also modified. The new method provides for a more consistent removal of dust after pellet removal from the test bed before the start of the next run. The relatively short run durations for the initial testing was also found to be a potential problem and that a much longer duration would give the susceptible pellets time to degrade and for dust particles to migrate to the bed outlet screens before the end of the run.

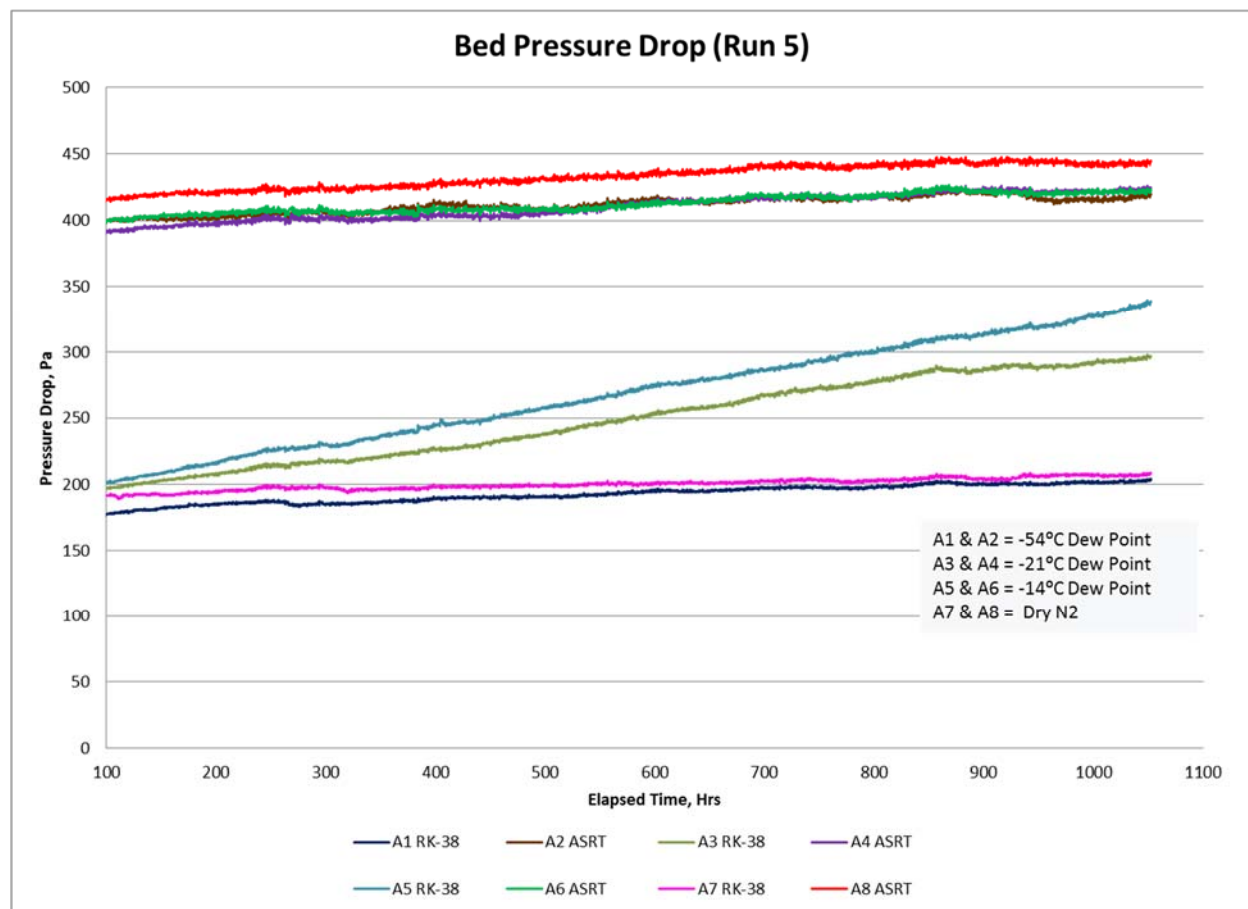


Figure 8. Differential Pressure across Test Beds during 1056 Hour Run

Figure 8 shows the pressure drop over the duration of the run that was performed after the test bed redesign. The test run lasted 1056 hours, which is the thermal cycle equivalent of ≈ 87 days of ISS CDRA operations. The plots show that, for the RK-38 material, there is clear correlation between the increase in pressure drop and the humidity of the process gas. Since the RK-38 and ASRT materials have different pellet shapes and packing characteristics, the initial pressure drop for the ASRT is nearly twice that of the RK-38. However, as the figure shows, there was minimal increase in the pressure drop across any of the ASRT beds. A numerical analysis of the data indicated that the increase in pressure was linear in nature and relatively constant over the duration of the run for all of the humidity cases.

Table 4 shows a compilation of the results for the test run. The rate of pressure increase is normalized to percent increase per 1000 hours of HST operation. The pressure across the test beds containing the ASRT increased 5% to 10% per 1000 hours but no correlation with inlet humidity is apparent. For the RK-38 material however, the correlation is evident. For the RK-38 bed with the driest inlet stream the pressure increase is similar to that of the ASRT beds, for the wetter cases the increase is significantly higher.

Table 4. Test Bed Pressure Change per 1000 Hours of Cyclic Operations

Inlet H ₂ O pp, mmHg	RK-38 Bed Pressure Drop		ASRT Bed Pressure Drop	
	Initial Pressure, Pa	Pressure Increase, % /1000 Hours	Initial Pressure, Pa	Pressure Increase, % /1000 Hours
$< 1 \times 10^{-5}$	190	9.2	413	8.23
0.012	177	15.0	399	5.64
0.70	185	62.8	389	9.49
1.38	188	74.5	397	6.65

The HST test article assemblies include a downstream filter with a 2 μm pore size to catch any dust that passes through the 50 μm bed outlet screen. Figure 9 shows the pressure across the filters. No statistically significant increase could be identified for any of the assemblies. The filters are sintered stainless steel and have a large surface area. Due to this, the lack of measurable increase does not necessarily mean that no fine dust was captured but rather that the amount was too small to be measured by the resolution of the instrumentation. These results do indicate that generated dust particles are primarily larger than 50 μm .

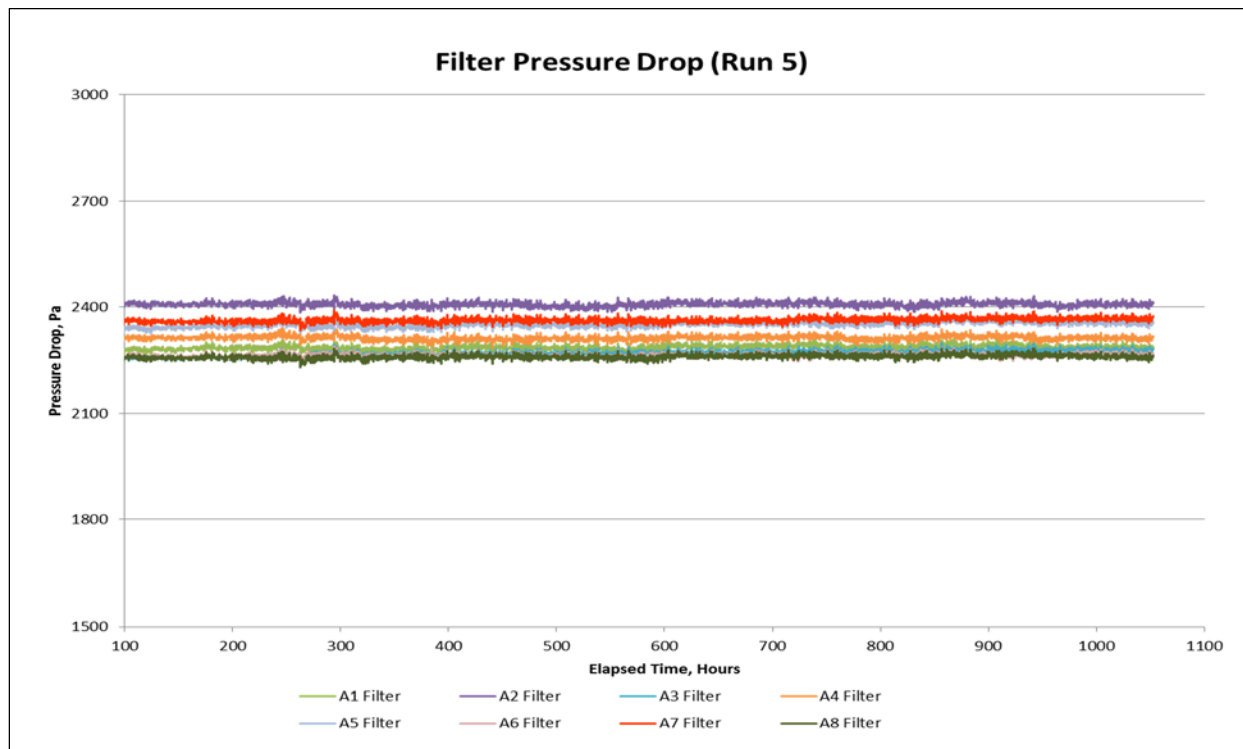


Figure 9. Differential Pressure across 2 μm Filter during 1056 Hour Run

VI. Conclusion and Future Work

The HST was developed to provide the unique capability for assessing the susceptibility of sorbent materials to degradation when subjected to thermal cycling under other than dry conditions. The results of the testing so far validate the on-orbit observation that the RK-38 sorbent can degrade faster than the ASRT material. The test results also show that the accelerated degradation can be correlated to increased humidity of the process gas. Data from the on-orbit CDRA operations indicate that the humidity of the gas entering the sorbent beds is sometimes higher than design levels and the findings of the HST help explain the observed faster than expected pressure rise.

Operations on the HST stand are continuing with the same samples of ASRT and RK-38 documented herein. The objective of this extended testing is to determine if the material degradation trends continue at the initial rates or if they change over time. Once this determination has been made, the test sequence will be terminated and the test stand readied for a test sequence to evaluate alternative ISS CDRA sorbents. The sorbent pellets removed from the test assemblies during the HST cyclic testing are undergoing strength testing and the results were unavailable for this paper. When complete, the results of the strength tests will be merged with the HST pressure drop data to provide a more complete analysis of the hydrothermal stability of the materials.

Future regenerative air revitalization systems are expected to utilize a temperature-swing process much like that of the current ISS CDRA implementation. The results of the HST show that a test to verify the hydrothermal stability of any sorbent candidate should be included when assessing the suitability for use in future closed-loop life support systems.

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